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Carbon nanotubes have received extraordinary attention, in part because of their unique mechanical and electronic properties. Despite an enormous number of studies concerning their properties and potential applications, relatively little is known regarding the mechanisms by which they nucleate and grow. This is presently the predominant reason that their application is not widespread: we cannot make them either efficiently enough to yield high volume / low cost materials or with sufficient control for applications in electronics.

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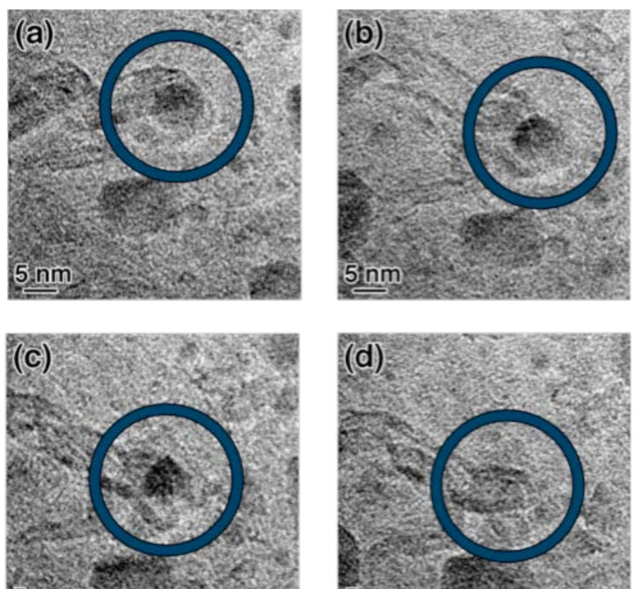
The Birth, Life and Death of the CNT: Imaging Carbon Nanotube Growth

PI: Eric A. Stach, Purdue University

Carbon nanotubes have received extraordinary attention, in part because of their unique mechanical and electronic properties. Despite an enormous number of studies concerning their properties and potential applications, relatively little is known regarding the mechanisms by which they nucleate and grow. This is presently the predominant reason that their application is not widespread: we cannot make them either efficiently enough to yield high volume / low cost materials or with sufficient control for applications in electronics.

The primary reason that we lack this understanding is because of the difficulties of finding appropriate characterization methods to quantify how these processes occur. The best technique to characterize individual nanotubes is transmission electron microscopy (TEM). However, TEM is generally a static imaging technique. During this STTR grant period we have optimized a unique new environmental-cell transmission electron microscope (E-TEM) at Purdue's Birck Nanotechnology Center to observe nanotube growth processes directly, at elevated temperature and pressure and with atomic level resolution. This development has included creation of appropriate sample geometries that mimic the catalyst substrate systems used for the growth of high-quality and high-density nanotube 'carpet' arrays and the reworking of the TEM vacuum and gas manifold systems to yield conditions for controlled nanotube synthesis. At the end of the grant period, we were in a position where nanotube nucleation and growth visualization is a routine accomplishment.



Real time images of nanotube growth and termination, acquired at 650°C in 2.5 mTorr C_2H_2 and 7.5 mTorr H_2.

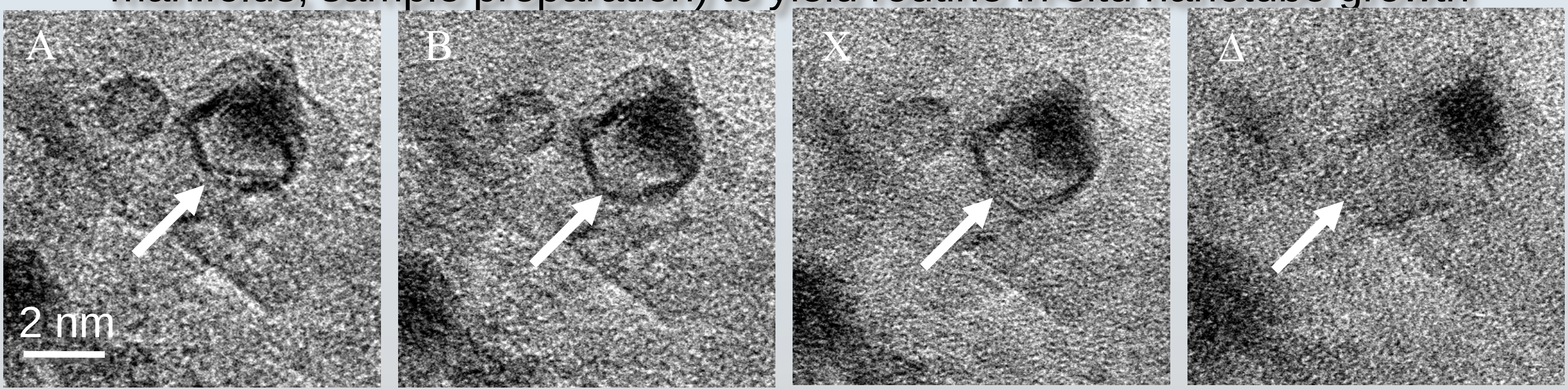
The catalyst that is circled coarsens via the Ostwald ripening process.

We have utilized these observations to understand a number of phenomena associated with nanotube growth. Perhaps most importantly, during the course of early, unsuccessful experimentation we noticed that the catalysts responsible for nanotube nucleation exhibited a strong tendency to coarsen via the Ostwald ripening mechanism. In this mechanism, larger particles grow at the expense of smaller ones, as the large ones have a lower chemical potential due to their smaller surface free energy.

Working with the Hauge group at Rice and Dr. Benji Maruyama at WP-AFRL, we have systematically demonstrated that Ostwald ripening was a mechanism by which nanotube growth terminates, and that catalyst conditioning via both atomic hydrogen exposure and controlled water vapor incorporation during growth leads to substantially longer nanotube growths. These systematic observations were correlated with in-situ observations (such as those shown here) of catalyst coarsening at the termination of growth. These results have important ramifications on creation of high yield nanotube carpet arrays: systems of interest for applications such as field emission and for interconnecting polymer composite laminates.

Observing nanotube nucleation & growth

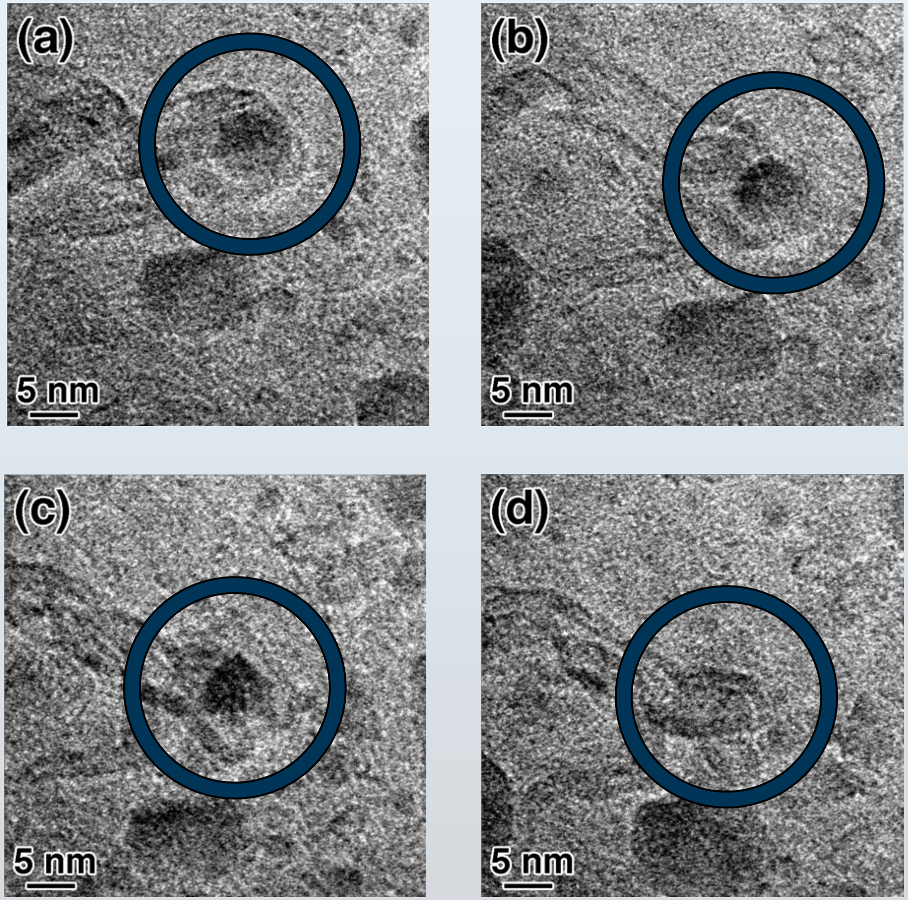
- Understanding nanostructure synthesis requires real time observations of nucleation, growth and growth termination.
- We utilize a unique new transmission electron microscope to watch growth processes as they happen, at temperature, pressure and atomic resolution.
- During the grant period we optimized the system (microscope, gas manifolds, sample preparation) to yield routine in-situ nanotube growth



Plan view TEM image of nanotube nucleation and growth. Rapid extension of the tube between images C & D is correlated with catalyst liquefaction, as reflected in poorer image conditions.

Understanding nanotube growth termination

- Carbon nanotubes have great promise as reinforcing elements in advanced composites.
- However, it is difficult to create tubes greater than a couple of millimeters in length.
- Using real time imaging of nanotube growth, we have shown that growth termination is caused by catalyst coarsening via the Ostwald ripening mechanism.
- These results are correlated with careful growth studies at Rice and the WP-AFRL that clarify the role of water on inhibiting catalyst coarsening.



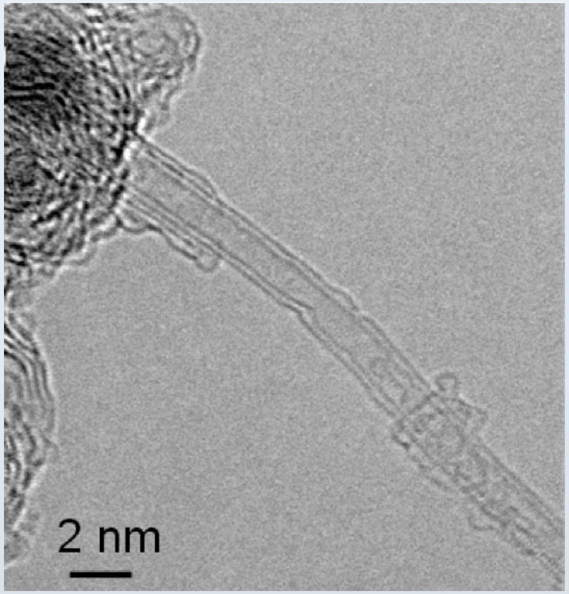
Real time images of nanotube growth and termination, acquired at 650°C in 2.5 mTorr C_2H_2 and 7.5 mTorr H_2.

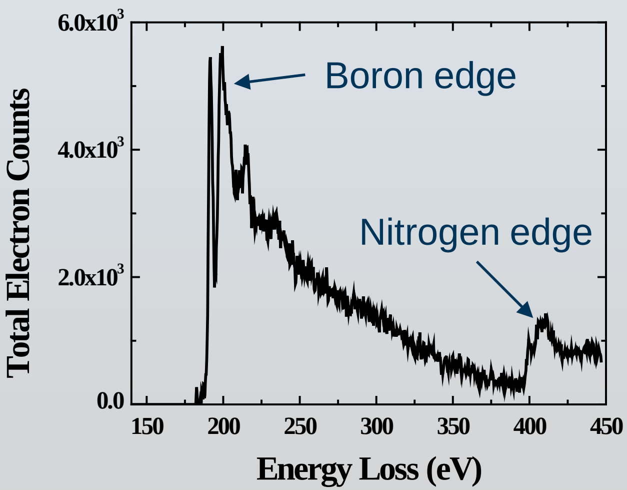
The catalyst that is circled coarsens via the Ostwald ripening process.

P.B. Amama, et al., *Role of Water in Super Growth of Single-Walled Carbon Nanotube Carpets.* Nano Lett., **9**(1) 44-49, 2009.

Scalable synthesis of BN nanotubes

- Boron nitride nanotubes have invariant electronic properties and high oxidation resistance.
- Synthesis using borazine, ammonia and a floating nickelocene catalyst performed at Sneddon Lab at U Penn and WP-AFRL
- Transmission electron microscopy images reveal creation of high quality double-walled tubes.
- Electron energy loss spectroscopy confirms that the tubes are free of carbon.
- The synthesis method is scalable, dramatically increasing the number of applications and utility of these structures.





M. J. Kim, et al., *Δουβλε–ωαλλεδ βορον νιτριδε νανοτυβεσ γροων βψ φλοατινγ χηεμιχαλ ϖαπορ δεποσιτιον,* Nano Letters, **8**(10), 3298-3302,